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(54) Methanol from synthesis gas

(57) A method of producing methanol from synthesis gas containing for example 60—80% by volume of H₂, 5—25% by volume of CO, 3—10% by volume of CO₂, up to 5% by volume of CH₄ and up to 1.5% by volume of N₂, comprises passing the gas at a pressure of 40—110 atm and a

temperature of 160—300°C through a catalyst containing the oxides of copper, and zinc and either aluminium or chromium with manganese addition, wherein the content of individual oxides in weight per cent are as follows: 20—50% copper oxide, 15—60% zinc oxide, 5—35% alumina, 5—35% chromium oxide and 0, 2—7% manganese oxide.

GB2 025 418 A

SPECIFICATION

Method for producing methanol

This invention relates to a method of producing methanol by catalytic synthesis from carbon monoxide and dioxide with hydrogen.

5 Previously proposed processes involve hydrogenation in recirculating systems in which gaseous mixtures containing hydrogen, carbon monoxide and carbon dioxide are passed at a temperature of from 200 to 300°C under a pressure of from 30 to 150 atmospheres through a catalyst bed, normally a copper — zinc — aluminum catalyst. The reaction gases are cooled in a condenser to recover the liquid products since a single passage through the catalyst is insufficient to complete the hydrogenation reaction, the unreacted gases are supplemented by the addition of fresh gas and recycled through the synthesis reactor. Precise temperature control is required in the catalyst bed, because it has a significant influence on the yield of the process and the quantity of by products obtained. The hydrogenation reaction is strongly exothermic in character, and during the passage of the reaction mixture through the catalyst the temperature and partial pressures of the components not participating in the reaction gradually increase.

The commonly used catalysts, containing zinc chromate, are adequately active at temperatures above 300°C to give a sufficiently high rate of reaction between the carbon mono and dioxide and hydrogen. However, the thermodynamic equilibrium state is so disadvantageous, that reaction is obtainable only at pressures over 2000 atmospheres.

20 The catalysts, containing copper as well as zinc and chromium have a catalytic effect on the methanol synthesis reactions at temperatures of from 200 to 300°C, so the process can be carried out at lower pressures, e.g. at from 50 to 100 atmospheres.

The disadvantages of these catalysts are that they can be in a very narrow temperature range and have an active life of less than 10,000 hrs. Although it is possible to select the reaction conditions, i.e. the temperature, pressure, gas composition and loading in order that the methanol yield is obtained at least 1 kilogram per litre of catalyst per hour, the amount of heat generated is so great that the copper catalysts age more rapidly because of irreversible recrystallization of the catalyst component, resulting in significant shortening of its life and activity.

30 According to the present invention there is provided, a method of producing methanol from a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen, comprising passing the synthesis gas at a pressure of from 40 to 110 atm and a temperature of from 160 to 300°C through a catalyst containing from 20 to 50 % by weight of copper oxide; from 15 to 60 % by weight of zinc oxide; from 5 to 35 % by weight of alumina or chromium oxide and from 0.2 to 7 % by weight of manganese oxides.

35 The synthesis gas typically contains: 60—80 % H₂, 5—25 % CO, 3—10 % CO₂, up to 5 % CH₄ and up to 15 % N₂, and preferably containing: 71 % H₂, 18.5 % CO, 5.5 % CO₂, 2 % CH₄ and 3.0 % N₂. Preferably the temperature is increased gradually from 140 to 180°C and pressure to 30 atmospheres and the gas volumetric speed to 10,000 NL/1_k . h to obtain the active catalyst form. The reduction speed is determined by means of the quantity of separated water and of temperature in the catalyst zone.

40 Afterwards, having established the required catalyst work parameters, the mixture is proportioned onto the catalyst bed, containing copper, zinc, aluminum and manganese, or copper, zinc, chromium and manganese, under the pressure of 30—110 atmospheres at temperature of 160—300°C, with volumetric speed of 5000—50,000 h⁻¹. The catalytic activity, measured at predetermined time intervals and expressed in kilograms of 100 % concentrated methanol per 1 kg of the catalyst and 1 hour, for established work parameters is presented in tables 1 and 2. The catalyst used in the method of invention, containing 20—50 weight percent of copper oxide, 15—60 % of zinc oxide, 5—35 % of alumina, 5—35 % of chromium oxide and 0.2—7 % of manganese oxides, may be obtained as coprecipitation product by the addition of sodium carbonate or hydroxide to a copper, zinc, aluminum, chromium and manganese nitrate solution at elevated temperature, the solution containing at least two of the nitrates simultaneously, while temperatures of a nitrite solution and precipitation solution are equal within the range of 80—100°C. The concentration of precipitating solution is preferably 5—10 weight percent, and the nitrate solution is preferably 10—15 wt. pct. calculated for the total amount of nitrates, and the final pH value is between 8 and 9. The sediment rinsed to a neutral reaction is dried at 270—300°C, granulated with addition of 2 wt. pct. graphite and then manganese, as an aqueous solution of hypermanganic acid, having concentration of 2—10 wt. pct. is delivered into the catalytic system and the product is finally dried and pelletized. The proportioning rate of the precipitating agent is within the range of 30—50 litres per hour during the catalyst precipitation.

By the method according to the invention, the methanol production process can be performed in one step with gas recirculation after liquefaction and separation of a liquid product, or in several steps with methanol separation between the steps. The carrying out of the process according to the invention increases the yield, which according to former processes amounts to about 0.35—0.60 kg of 100 % concentrated methanol for 1 kg of the catalyst during 1 hour, while according to the invention it is obtainable 0.9 kg of 100 % concentrated methanol for 1 kg of the catalyst an hour. The use of a catalyst, containing copper, zinc, aluminum and manganese, or copper, zinc, chromium and manganese,

improves significantly the reaction parameters and decreases the processing pressure and temperature, which are of important influence on the catalyst life. The catalyst life in the method according to the invention can be as high as two years. The crude methanol obtained by the method of invention contains some organic compound impurities, such as higher alcohols, ethers and paraffins, in an amount of up to 1 wt. pct.

EXAMPLE

A quantity of 100 grams of catalyst containing 32,4 wt. % CuO, 44,3 wt. % ZnO, 22,3 wt. % Al_2O_3 and 1 wt. % MnO; is introduced to a reactor of 16 mm diameter and 600 mm length, a synthesis gas, containing 71 % H_2 , 18,5 % CO, 5,5 % CO_2 , 2,0 % CH_4 and 3,0 % N_2 , is passed at a volume rate of 5000—10000 h^{-1} through catalyst the temperature being raised gradually from 140 to 180°C and at a pressure up to 30 atmospheres, in order to obtain the active form of the catalyst. The same gaseous mixture is proportioned at the pressure of 50 atm and temperature 180°C at a volume rate of 20,000 $\text{Ni}/1 \text{ cat—hour}$.

The crude methanol obtained contains: 90 % CH_3OH , 9,2 % H_2O and 0,8 % of organic impurities, mainly methyl formate, acetone, ethanol and higher alcohols.

In Tables 1 and 2 are shown the activities of different catalysts, expressed in kilograms of 100 % concentrated methanol per 1 kg of catalyst an hour at determined technological parameters.

TABLE 1

Temperature = 180°C, Pressure = 50 atm, Volume Rate 20000 h⁻¹Gas Analysis: 67,2 % H₂, 22,5 % CO, 5,5 % CO₂, 1,9 % CH₄, 2,5 % N₂

CATALYST (weight percent)	Catalyst age (in hours)					Remarks
	50	100	200	300	500	
	kg 100 % CH ₃ OH/kg cat hour					
CuO — 32,4 ZnO — 44,3 Al ₂ O ₃ — 22,3 MnO ₂ — 1,0	0,900	0,920	0,9100	0,920	0,930	Manganese introduced into catalyst system as HMnO ₄ during granulation of catalyst
CuO — 30,3 ZnO — 44,3 Al ₂ O ₃ — 20,4 MnO — 5,1	0,600	0,800	0,800	0,805	0,795	Manganese introduced into catalyst system during precipitation from Cu, Zn, Al and Mn nitrate solution
CuO — 25,0 % ZnO — 50,0 Al ₂ O ₃ — 23,0 MnO — 2,0	0,930	0,950	0,960	0,945	0,960	Manganese introduced into catalyst system as manganous acetate during granulation of catalyst
CuO — 40,0 ZnO — 38,0 Cr ₂ O ₃ — 20,0 MnO — 2,0	0,750	0,800	0,805	0,800	0,795	Manganese introduced into catalyst system as manganous acetate during granulation of catalyst

TABLE 2

Temperature — 200°C, Pressure = 70 atm, Volume Rate = 20000 h⁻¹Gas Analysis 67,2 % H₂, 22,5 % CO, 5,5 % CO₂, 1,9 % CH₄, 2,5 % N₂

CATALYST (weight percent)	Catalyst age (in hours)					Remarks
	50	100	200	300	500	
	kg 100 % CH ₃ OH/kg cat per hour					
CuO — 32,4 ZnO — 44,3 Al ₂ O ₃ — 22,3 MnO ₂ — 1,0	1,080	1,150	1,100	1,250	1,200	Manganese introduced into catalyst system as HMnO ₄ during granulation of catalyst
CuO — 30,3 ZnO — 44,3 Al ₂ O ₃ — 20,4 MnO — 5,1	0,800	0,850	0,910	0,905	0,910	Manganese introduced into catalyst system during precipitation of catalyst from Cu, Zn, Al and Mn nitrate solutions
CuO — 25,0 ZnO — 50,0 Al ₂ O ₃ — 23,0 MnO — 2,0	0,950	1,170	1,205	1,180	1,200	Manganese introduced into catalyst system as manganous acetate during granulation of catalyst
CuO — 40,0 ZnO — 38,0 Cr ₂ O ₃ — 20,0 MnO — 2,0	0,850	0,900	0,905	0,900	0,895	Manganese introduced into catalyst system as manganous acetate during granulation of catalyst

CLAIMS

1. A method of producing methanol from a synthesis gas containing carbon monoxide, carbon dioxide and hydrogen, comprising passing the synthesis gas at a pressure of from 40 to 110 atm and a temperature of from 160 to 300°C through a catalyst containing: from 20 to 50 % by weight of copper oxide; from 15 to 60 % by weight of zinc oxide; from 5 to 35 % by weight of alumina or chromium oxide and from 0,2 to 7 % by weight of manganese oxides.
2. A method according to claim 1, in which the catalyst contains alumina.
3. A method according to claim 1, in which the catalyst contains chromium oxide.
4. A method according to claim 1 or 2 or 3 wherein the synthesis gas contains: from 60 to 80 % of hydrogen from 5 to 25 % of carbon monoxide, from 3 to 10 % of carbon dioxide; up to 5 % of methane and up to 15 % of nitrogen.
5. A method of producing methanol, according to claim 1, substantially as hereinbefore described.
6. Methanol whenever produced by the method claimed in any of claims 1 to 5.

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